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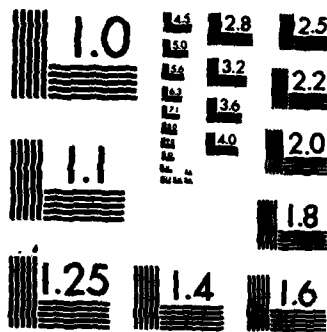
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AEROSOL DIRECT FLUORINATION: SYNTHESSES OF THE PERFLUOROALKYL
ORTHOCARBONATES, F-TETRAMETHYL AND F-ETHYLENE ORTHOCARBONATES

by

James L. Adcock* and
Mark L. Robin

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

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by

James L. Adcock* and
Mark L. Robin

Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

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The extension of aerosol direct fluorination techniques to the syntheses of perfluoroalkyl orthocarbonates from the analogue alkyl orthocarbonates is described. These perfluorinated compounds, F-tetramethyl orthocarbonate and F-ethylene orthocarbonate have not been previously prepared by any other method. They are stable, relatively unreactive and highly volatile. The orthocarbonates are acid sensitive and like ketals can be fluorinated without decomposition only under the low acidity conditions which prevail in the aerosol direct fluorination system. The unoptimized yields of F-tetramethyl orthocarbonate and F-trimethyl orthoformate the major products in the fluorination of tetramethyl orthocarbonate are 8% and 19.2% respectively, and make up 30% and 59% respectively of the total product collected. F-ethylene orthocarbonate fragments less and can be produced in 98% purity and a 17% theoretical yield based on the total amount of ethylene orthocarbonate injected.



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Aerosol Direct Fluorination: Syntheses of the Perfluoroalkyl
Orthocarbonates, F-Tetramethyl and F-Ethylene Orthocarbonates

by

J. L. Adcock and M. L. Robin
Department of Chemistry
Knoxville, Tennessee 37996-1600

The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.^{1,2} The application of this process to alkanes, ethers, cycloalkanes, ketals, and ketones has been demonstrated.¹⁻⁴ The extension of this novel process to orthocarbonates provides direct access to analog perfluoroalkyl orthocarbonates, a feat not realized by presently available fluorination methods. We report here the first syntheses of the perfluoroalkyl orthocarbonates, which are obtained in modest yields via the aerosol direct fluorination of the corresponding hydrocarbon⁵.

A small number of trihydriperfluoroalkyl orthocarbonates, $(R_fCH_2O)_4C$, where $R_f = H(CF_2)_n$ ($n = 2,4,6$) have been synthesized via the reaction of the corresponding fluoro alcohols with carbon tetrachloride in the presence of a ferric chloride catalyst. These trihydriperfluoroalkyl orthocarbonates have found use as hydraulic fluids, heat-exchange fluids, lubricants, and dielectric fluids.^{5,6} The perfluoroalkyl orthocarbonates are not accessible via this route however; the perfluoro alcohols R_fCF_2OH are not available, due to the instability of the $-CF_2OH$ system to the loss of hydrogen fluoride.⁷ The related compounds, the perfluoroalkylthio orthocarbonates, $(R_fS)_4C$, are available via the reaction of a perfluoroalkylthio metal compound with tetrabromomethane, and have found use as solvents for difficultly soluble polymers such as low molecular weight tetrafluoroethylene polymer.^{8,9}

Results and Discussion

The major products collected from the aerosol direct fluorination of tetramethyl orthocarbonate were F-trimethyl orthoformate and F-tetramethyl orthocarbonate, which constituted 59% and 30% of the total products collected by weight, respectively. The aerosol system is dependent on the generation of a particulate aerosol which is ideally crystalline, of uniform size and with little tendency to aggregate. If the conditions for producing the aerosol are ideal, percent yields based on throughputs and product percent distributions will differ by only a few percent; as molecules deviate from this ideality, the percent yields based on throughput fall due to physical losses within the aerosol generator and initial reaction stage (see Reference 1). These losses can be significant and result in sometimes significant amounts of unfluorinated or complex mixtures of generally less than trifluorinated products collected at the close of the reactions when the reactor warms to ambient or is opened for cleaning between reaction runs. If no corrections or adjustments are made due to recovered unreacted or partially reacted materials, the yield of F-tetramethyl orthocarbonate was 8%. The major product from the aerosol direct fluorination of tetramethyl orthocarbonate was F-trimethyl orthoformate (in 19.2% yield) which results from the cleavage of one of the methoxy groups.

The major product collected from the aerosol direct fluorination of ethylene orthocarbonate was F-ethylene orthocarbonate which was produced in a 17% yield. The -78°C vacuum line fraction contained the majority of the F-ethylene orthocarbonate produced in 98% purity. It should be noted that significant amounts of unreacted ethylene orthocarbonate, which could be recovered, were found upon opening the reactor for cleaning.

The usual routes to orthocarbonates are not applicable in the case of the perfluoroalkyl orthocarbonates, and their synthesis has not been previously reported. Hydrocarbon orthocarbonates are typically prepared by the action of sodium alkoxides on trichloronitromethane (chloropicrin).¹⁰ While fluorinated alkoxides are known, difficulties arise in their use in synthesis due to the fact that the perfluorinated alkoxides are very weak nucleophiles; are highly dissociated or undergo competing side reactions at the temperatures necessary for reaction.¹¹ As previously mentioned, orthocarbonates of the general formula $(R_fCH_2O)_4C$ are available via the reaction of fluoroalcohols with carbon tetrachloride, but the perfluoroalkyl orthocarbonates, $(R_fO)_4C$, are unattainable via this method due to the instability of the perfluoro alcohols, R_fCF_2OH .

Experimental

The basic aerosol fluorinator design and a description of the process are presented elsewhere.¹ A modified aerosol generator, adapted to an evaporator/sublimator unit, was employed in the reactions.⁴ Details of the aerosol fluorination parameters are given in Table 1. Tetramethyl orthocarbonate was fed into the evaporator/sublimator unit via a 5 mL Precision Sampling Corp, "Pressure Lok" syringe. In the case of ethylene orthocarbonate, the evaporator/sublimator was filled with the solid ethylene orthocarbonate. Workup of products following removal of hydrogen fluoride consisted of vacuum line fractionation, infrared assay of fractions, gas chromatographic separation of components using a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed Chromosorb P conditioned at 225°C (12 h). Following gas chromatographic separation (Bendix Model 2300, subambient multicontroller) products were collected, transferred to the vacuum line, assayed, and characterized by vapor phase

infrared spectrophotometry (PE 1330), electron impact (70 eV) and chemical ionization (methane plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A computer) and ^{19}F nuclear resonance (JEOL FX90Q, omniprobe) in CDCl_3 with 1% CFCl_3 internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reagents. Tetramethyl orthocarbonate (99%, Aldrich) was used as received. Ethylene orthocarbonate was prepared via the reaction of tetramethyl orthocarbonate with ethylene glycol in the presence of p-toluenesulfonic acid.¹²

F-Tetramethyl orthocarbonate. A pump speed corresponding to 3.9 mmol/h was established and 2.9 mL of tetramethyl orthocarbonate delivered over a 5.7 h period. From the crude product (2.08 g) was isolated 0.63 g (30%) pure F-tetramethyl orthocarbonate (GLC temperature program: -35° , 7 min; $2^\circ\text{C}/\text{min}$ to 0°C , 1 min; $15^\circ\text{C}/\text{min}$ to 180°C) corresponding to a percent yield of 8% based on total tetramethyl orthocarbonate injected. $(\text{CF}_3\text{O})_4\text{C}$: IR (cm^{-1}) 1320 (vs), 1260 (vs), 1225 (s), 1215 (vs), 1100 (vs), 920 (m), 885 (w), 730 (m); major mass cations were $[\text{m}/\text{e}(\text{int.})\text{formula}]$: [EI] 267(8) $\text{C}_4\text{F}_9\text{O}_3$, $\text{M}-\text{OCF}_3$; 113(5) $\text{C}_2\text{F}_3\text{O}_2$; 69(100) CF_3 ; [CI] 267(100) $\text{C}_4\text{F}_9\text{O}_3$; 101(6) $\text{C}_2\text{F}_4\text{H}$; 69(56) CF_3 ; NMR δ = -56.67 ppm (s); Elemental Analysis: Calculated for $\text{C}_5\text{F}_{12}\text{O}_4$, C 17.06, F 64.76; Found C —.—, F —.—. Also isolated from the reaction were 1.24 g (19.2% yield) F-trimethyl orthoformate. $(\text{CF}_3\text{O})_3\text{CF}$: IR (cm^{-1}) 1320 (s), 1300 (vs), 1230 (vs), 1175 (m), 1120 (vs), 1105 (vs), 910 (m), 730 (m); major mass cations were $[\text{m}/\text{e}(\text{int.})\text{formula}]$: [EI] 204(21) $\text{C}_3\text{F}_8\text{O}$, 69(100) CF_3 , 47(2) CFO ; ^{19}F NMR resonances occur at δ_{CF_3} = -57.14 ppm (d), δ_{CF} = -58.85 ppm (dectet), $J_{\text{CF}_3-\text{CF}}$ = 9.76 Hz.

F-Ethylene orthocarbonate. Ethylene orthocarbonate (2.06 g) was loaded into the sublimator. The sublimator was maintained at a temperature of

125°C throughout the 4 hours duration of the run. The reaction was stopped, and upon opening the reactor 0.89 g of unreacted ethylene orthocarbonate was recovered. The crude products were fractionated through -78°C and -123°C cold traps and 0.35 g (98%) pure F-ethylene orthocarbonate isolated from the -78°C trap (GLC temperature program: -20°C, 5 m; 5°C/m to 0°C for 1 m; 5°C/m to 180°C). An additional 0.06 g F-ethylene orthocarbonate were recovered from the -123°C trap. The percent yield of F-ethylene orthocarbonate was 17%, based on the throughput of ethylene orthocarbonate, $\text{OCF}_2\text{CF}_2\text{O}-\text{C}-\text{OCF}_2\text{CF}_2\text{O}$: IR (cm^{-1}) 1235 (s), 1170 (s), 1130 (vs), 1090 (m), 1030 (m), 820 (w), 760 (m), 730 (m); major mass cations [$m/e(\text{int.})$ formula]: [EI] 210(2) $\text{C}_4\text{F}_6\text{O}_3$, $\text{M}-\text{COF}_2$; 144(14) $\text{C}_3\text{F}_4\text{O}_2$, 119(3) C_2F_5 , 100(100) C_2F_4 , 97(24) $\text{C}_2\text{F}_3\text{O}$; 69(20) CF_3 ; 50(21) CF_2 , 47(6) CFO : [CI] 210(1) $\text{C}_4\text{F}_6\text{O}_3$, 162(100) $\text{C}_3\text{F}_4\text{O}_3\text{H}$, 119(9) C_2F_5 , 117(9) $\text{C}_2\text{F}_4\text{OH}$, 101(11) $\text{C}_2\text{F}_4\text{H}$, 100(63) C_2F_4 , 97(14) $\text{C}_2\text{F}_3\text{O}$, 69(15) CF_3 ; ^{19}F NMR resonance occurs at $\delta = -87.68$ ppm (s); Elemental Analysis: Calculated for $\text{C}_5\text{F}_8\text{O}_4$; C 21.76, F 55.06; Found C ---, F ---.

Acknowledgement

This work was supported in part by the Office of Naval Research whose support is gratefully acknowledged. Earlier support by the Research Corporation, Cottrell Research Fund, is also acknowledged.

TABLE 1
TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS^a

| Starting Compound | Fluorine Flow mL/m Reactor Mod. 1 Mod. 2 | | Helium Diluent mL/m Reactor Mod. 1 Mod. 2 | | Reaction Temp. °C Reactor Mod. 1 Mod. 2 | | Main Helium Carrier mL/m | Hydrocarbon Throughput millimoles/hr (H.C. carrier) | Overall ^b Stoichlo- metry Hc:F ₂ | Percent F ₂ Conc. Final Stage | Reac- tion Time Sec. | Product Distribu- tion % Collected | Product Yield % Theoret- ical |
|---------------------------|---|----|--|-----|--|-----|-----------------------------|--|---|---|-------------------------------|---|--|
| Tetramethylorthocarbonate | 10 | 20 | 30 | 150 | 150 | 150 | 550 | 3.9 ^d | 1:38 | 3.7% | 50 | 30% | 8% |
| Ethylene orthocarbonate | 20 | 20 | — | 150 | 150 | 150 | 800 | 2.2 ^e | 1:44 | 2.0% | 40 | 98% | 17% |

^aSee references 1 and 4 for the significance of these parameters.

^bOne milliliter/minute F₂ delivers 2.44 mmol/h F₂.

^cReactor volume/total flows; reactor volume = 1355 cc.

^dTotal evaporator flow = 550 mL/m (500 mL/m primary, 50 mL/m secondary).

^eTotal evaporator flow = 750 mL/m (700 mL/m primary, 50 mL/m secondary).

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